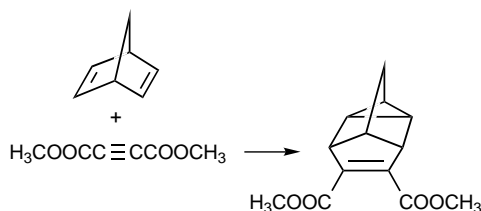


## cycloaddition

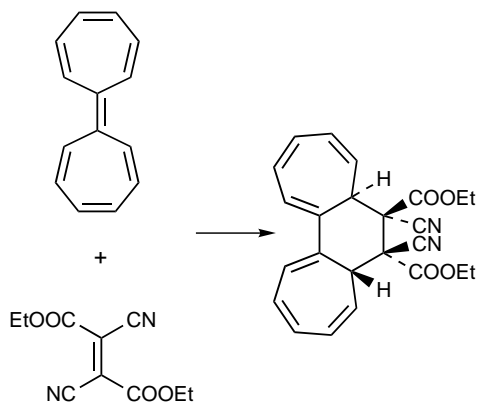
A reaction in which two or more unsaturated molecules (or parts of the same molecule) combine with the formation of a cyclic *adduct* in which there is a net reduction of the bond multiplicity.

The following two systems of notations have been used for the more detailed specification of cycloadditions, of which the second, more recent system [described under (2)] is preferred:

(1) A  $(i + j + \dots)$  cycloaddition is a reaction in which two or more molecules (or parts of the same molecule), respectively, provide units of  $i, j, \dots$  linearly connected atoms: these units become joined at their respective termini by new  $\sigma$ -bonds so as to form a cycle containing  $(i + j + \dots)$  atoms. In this notation, (a) a Diels–Alder reaction is a  $(4+2)$  cycloaddition, (b) the initial reaction of ozone with an alkene is a  $(3+2)$  cycloaddition, and (c) the reaction shown below is a  $(2+2+2)$  cycloaddition. (N.B.: parentheses (...) are used in the description based on numbers of atoms.)



(2) The symbolism  $[i + j + \dots]$  for a cycloaddition identifies the numbers  $i, j, \dots$  of electrons in the interacting units that participate in the transformation of reactants to products. In this notation the reaction (a) and (b) of the preceding paragraph would both be described as  $[2+4]$  cycloadditions, and (c) as a  $[2+2+2]$  cycloaddition. The symbol *a* or *s* (*a* = antarafacial, *s* = suprafacial) is often added (usually as a subscript after the number to designate the stereochemistry of addition to each fragment. A subscript specifying the orbitals, *viz.*,  $\sigma$ ,  $\pi$  (sigma, pi) with their usual significance) or *n* (for an orbital associated with a single atom only), may be added as a subscript before the number. Thus the normal Diels–Alder reaction is a  $[4_s + 2_s]$  or  $[\pi 4_s + \pi 2_s]$  cycloaddition, whilst the reaction:



would be a  $[14_a + 2_s]$  or  $[\pi 14_a + \pi 2_s]$  cycloaddition. (N.B. Square brackets [...] are used in the descriptions based on numbers of electrons.)

Cycloadditions may be *pericyclic reactions* or (non-*concerted*) *stepwise reactions*. The term ‘dipolar cycloaddition’ is used for cycloadditions of 1,3-dipolar compounds.

See also *cheletropic reactions*.

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